OFFICE OF NAVAL RESEARCH

FINAL REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

ONR N00014-96-1-0733

FY 99PR01966-00

Combinatorial and Biomimetic Approach on Asymmetric Catalysis for the Synthesis of Ferroelectric Liquid Crystals

Xumu Zhang

The Pennsylvania State University
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Date Submitted: 2/28/2000

OFFICE OF NAVAL RESEARCH

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

R&T Number:

Contract/Grant Number: N00014-96-1-0733, FY98PR01966-00

Contract/Grant Title: Combinatorial and Biomimetic Approach on Asymmetric Catalysis for the Synthesis of Ferroelectric Liquid Crystals

Principal Investigator: Xumu Zhang

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a	Number of papers submitted to refereed journals, but not published:	0
b	Number of papers published in refereed journals:	10
c	Number of books or chapters submitted, but not yet published:	0
d	Number of books or chapter published:	0
e	Number of printed technical reports/non-refereed papers:	0
f	Number of patents filed:	7
g	Number of patents granted:	0
h	Number of invited presentations:	25
I	Number of submitted presentations:	5
j	Honors/Awards/Prizes for contract/grant employees:	4

k Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number:

Graduate Students:	1	Post-Doctoral Associates:	2
Including the number of,			
Female Graduate Students:	1	Female Post-Doctoral Associates:	1
the number of Minority Graduate students:	0	Minority Post-Doctoral Associates:	0
the number of Asian Graduate students:	1	Asian Post-Doctoral Associates:	2

l. Other Funding

Date:	May 1996 – April 1999
Title:	"Combinatorial and Biomimetic Approach on Asymmetric Catalysis for the Synthesis of Ferroelectric Liquid Crystals"
Submitted to:	Office of Naval Research, Young Investigator Award Program
Amount:	$375,000

In Progress

Date:	August 1997 – July 2000
Title:	"Asymmetric Synthesis Based on Chiral Heterobicyclo[2.2.1]heptanes"
Submitted to:	National Science Foundation
Amount:	$270,000

Date:	January 1998 – December 2001
Title:	"Asymmetric Catalysis for the Synthesis of Chiral Pharmaceuticals"
Submitted to:	Catalytica Inc.
Amount:	$360,000

Date:	July 1998 – June 2000
Title:	"Asymmetric Catalysis Based on New Chiral Ligands"
Submitted to:	The Camille and Henry Dreyfus Foundation: Dreyfus Teacher-Scholar Award
Amount:	$60,000

Date:	October 1998 – September 2001
Title:	"Nonlinear Optical Fiber Arrays for Optical Limiting Applications"
Submitted to:	US Navy/Naval Air Development Center
Amount:	$487,064
Participation:	I. C. Khoo, Professor of Electrical Engineering, is another co-PI.

Date:	July 1999 – June 2004
Title:	"Asymmetric Reduction of Simple Ketones and Imines"
Submitted to:	National Institutes of Health
Amount:	$1,025,000

Proposed

Requested Date:	July 2000 – June 2002
Title:	"Asymmetric Catalysis Based on New Phosphine Ligands"
Submitted to:	Alfred P. Sloan Foundation
Amount:	$30,000

Date:	July 2000 – June 2005
Title:	"Asymmetric Carbon-Carbon Bond Forming Reactions"
Submitted to:	National Institutes of Health
Amount:	$1,200,000

Honors/Awards/Prizes for contract/grant employees

DuPont Young Faculty Award 8/1/96-7/30/99

The Camille and Henry Dreyfus Foundation Teaching Scholar Award, 7/1/98- 6/30/2000

PATENTS

1 "Catalytic Asymmetric Hydrogenation, Hydroformylation, and Hydrovinylation Via Transition Metal Catalysts with Phosphines and Phosphites," X. Zhang, U.S. Patent Application, filed May 18, 1999.

2 "New Ligands Based on Chiral 2-Amino-2'-hydroxy-1,1'-binaphthyl and Related Frameworks for Asymmetric Catalysis," X. Zhang, U.S. Provisional Patent, filed June 24, 1999.

3 "Asymmetric Catalysis Based Chiral Phospholanes and Hydroxyl Phospholanes," X. Zhang, US patent Application, 60/097,473, filed August 19, 1999.

4 "New Chiral Phospholanes, P, N ligands, N, N ligands, Biphenols and Chelating Phosphines for Transition Metal-Catalyzed Asymmetric Reactions," X. Zhang and D. Xiao, U. S. Provisional Patent Application, filed August 23, 1999.

5 "New Chiral Phosphines in Transition Metal-Catalyzed Asymmetric Reactions," X. Zhang, U. S. Provisional Patent Application, filed November 8, 1999.

6 "Asymmetric Hydrogenation Using Transition Metal Catalysts with Chiral Binaphane Ligands," X. Zhang and D. Xiao, U. S. Provisional Patent Application, filed November 14, 1999.

7 "Transition Metal-Catalyzed Reactions Based on Chiral Amine Oxazolinyl Ligands and Related Compounds" X. Zhang, U. S. Provisional Patent Application, filed November 15, 1999.

Paper Published

1 "Highly Enantioselective Hydrogenation of Cyclic Enol Acetates Catalyzed by a Rh-PennPhos Compound," D. Xiao, Q. Jiang, Z. Zhang, P. Cao, X. Zhang, *Angewandte Chemi International English Edition,* **1999**, *38*, 516.

2 "The First Tridentate Ligand for Catalytic Enantioselective Aza-Claisen Rearrangement of Allylic Imidates" Y. Jiang, J. M. Longmire, and X. Zhang, *Tetrahedron Letters,* **1999,** *40*, 1449.

3 "Ru-BICP Catalyzed Asymmetric Hydrogenation of Aromatic Ketones," P. Cao, and X. Zhang, *Journal of Organic Chemistry,* **1999**, 64, 2127.

4 "Highly Enantioselective Hydrogenation of Cyclic Enamides Catalyzed by a Rh-PennPhos Complex," Z. Zhang, G. Zhu, Q. Jiang, D. Xiao, and X. Zhang, *Journal of Organic Chemistry,* **1999**, *64*, 1774..

5 "Highly Efficient Asymmetric Synthesis of β-Aminoacid Derivatives via Rhodium-Catalyzed Hydrogenation of β-(Acylamino)acrylates" G. Zhu, Z., Chen, Z., and X. Zhang, *Journal of Organic Chemistry,* **1999**, *64*, 6907.

6 "Highly Enantioselective Cyclocarbonylation of Allylic Alcohols Catalyzed by Pd-1,4-bisphosphine Complexes" P. Cao, and X. Zhang, *Journal of the American Chemical Society,* **1999,** *121,* 7708.

7 "Rh-Hydroxyl Bisphospholane Catalyzed Highly Enantioselective Hydrogenation of Dehydroamino Acids and Esters," W. Li, Z. Zhang, D. Xiao and X. Zhang, *Tetrahedron Letters*, **1999**, *40*, 6701.

8 "Development of New Chiral P, N Ligands and Their Application in Cu-Catalyzed Enantioselective Conjugate Addition of Diethylzinc to Enones," X. Hu, H. Chen and X. Zhang, *Angewandte Chemi International English Edition,* **1999**, *38*, 3518.

9 "Synthesis of a Novel Chiral Binaphthyl Phospholane and its Application in the Highly Enantioselective Hydrogenation of Enamides," D, Xiao, Z. Zhang, X. Zhang, *Organic Letters*, **1999**, *1*, 1679.

10 "Developing a Chiral Toolbox for Asymmetric Catalytic Reactions," X. Zhang, *Enantiomer*, **1999**, *4*, 541.

SUBMITTED PRESENTATIONS

1 "Developing a Practical Chiral Toolbox for Asymmetric Catalytic Reactions," IBC's Second International Symposium: New Synthetic Methods Novel Chemistry Advancements for Effective Drug Development, Naples, April 17, 2000.

2 "Developing a Practical Chiral Toolbox for Asymmetric Catalytic Reactions," 32nd Great Lakes Regional Meeting, Fargo, N.D. June 5, 2000.

3 "Developing a Practical Chiral Toolbox for Asymmetric Catalytic Reactions," Abbott Lab, IL, June 7, 2000.

4 "Recent Advances in Catalytic Asymmetric C-C bond Forming Reactions" The 6th International Symposium for Chinese Organic Chemists (ISCOC-2000) Shanghai, China, July 28, 2000

5 "Developing a Practical Chiral Toolbox for Asymmetric Catalytic Reactions," The International Symposium of Organometallic Chemistry, Shanghai, China, July 26, 2000.

PRESENTATIONS

1 "Developing a Chiral Toolbox for Asymmetric Catalytic Reactions," Purdue University, West Lafayette, IN, January 28, 1999.

2 "Developing a Chiral Toolbox for Asymmetric Catalytic Reactions," Wayne State, Detroit, MI, January 29, 1999.

3 "Developing a Chiral Toolbox for Asymmetric Catalytic Reactions," Scripps Research Institute, La Jolla, CA, February 1, 1999.

4 "Developing a Chiral Toolbox for Asymmetric Catalytic Reactions," University of California, San Diego, La Jolla, CA, February 2, 1999.

5 "Developing a Chiral Toolbox for Asymmetric Catalytic Reactions," University of North Carolina, Chapel Hill, NC, February 4, 1999.

6 "Developing a Chiral Toolbox for Asymmetric Catalytic Reactions," University of Virginia, Charlottesville, VA, February 5, 1999.

6 "Developing a Chiral Toolbox for Asymmetric Catalytic Reactions," Iowa State University of Science and Technology, Ames, IA, March 1, 1999.

7 "Developing a Chiral Toolbox for Asymmetric Catalytic Reactions," University of Wisconsin-Madison, Madison, WI, March 2, 1999.

8 "Developing a Chiral Toolbox for Asymmetric Catalytic Reactions," Pharmacia & Upjohn, Kalamazoo, MI, May 11, 1999.

9 "Developing a Chiral Toolbox for Asymmetric Catalytic Reactions," Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, P. R. China, May 19, 1999.

10 "Chiral Technology, Present and Future," Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, P. R. China, May 26, 1999.

11 "Developing a Chiral Toolbox for Asymmetric Catalytic Reactions." School of Pharmaceutical Sciences, Beijing Medical University, Beijing, P. R. China, May 31, 1999.

12 "Chiral Technology, Present and Future," National Natural Science Foundation of China, Beijing, P. R. China, June 1, 1999.

13 "Developing a Chiral Toolbox for Asymmetric Catalytic Reactions," Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, P. R. China, June 3, 1999.

14 "Developing a Chiral Toolbox for Asymmetric Catalytic Reactions," Sepracor Inc., Marlborough, MA, July 9, 1999.

15 "Developing a Chiral Toolbox for Asymmetric Catalytic Reactions," The Organic Reactions and Processes Gordon Conference, Henniker, NH, July 11, 1999.

16 "Developing a Chiral Toolbox for Asymmetric Catalytic Reactions," International Symposium on Chiral Discrimination ISCD '99, Chicago, IL, July 25, 1999.

17 "Developing a Chiral Toolbox for Asymmetric Catalytic Reactions," The Dow Chemical Company, Midland, November 4, 1999.

18 "Developing a Chiral Toolbox for Asymmetric Catalytic Reactions," Pfizer, Groton, CT, November 11, 1999.

19 "Developing a Chiral Toolbox for Asymmetric Catalytic Reactions," ChiraSource'99, Philadelphia, PA, November 18, 1999.

20 "Developing a Chiral Toolbox for Asymmetric Catalytic Reactions,"Symyx, Santa Clara, CA, December 16, 1999.

21 "Developing a Chiral Toolbox for Asymmetric Catalytic Reactions," Maxdem, LA, CA, December 17, 1999.

22 "Developing a Practical Chiral Toolbox for Asymmetric Catalytic Reactions," The R. W. Johnson Pharmaceutical Research Institute, Spring House, PA, January 20, 2000.

23 "Developing a Practical Chiral Toolbox for Asymmetric Catalytic Reactions," Alanex, La Jolla, February 3, 2000.

24 "Developing a Practical Chiral Toolbox for Asymmetric Catalytic Reactions," Agouron, La Jolla, February 4, 2000.

25 "Practical Asymmetric Catalytic Hydrogenation Reactions" Informex 2000, New Orleans, LA, February 16, 2000.

Principal Investigator: Xumu Zhang
Phone Number: 814-865-4221
Cognizant ONR Program Officer Harold E. Guard/ Angela Ervin

Program Objective: Development of Efficient Asymmetric Catalysts for the Synthesis of Ferroelectric Liquid Crystals

Significant results during last year

During the funding period, we have made significant progress both in the developing new methods for asymmetric synthesis and discovering new liquid crystal materials. Several papers have been published (J. Am. Chem. Soc., J. Org. Chem. and Tetrahedral Letter). We have developed a chiral toolbox with a large set of chiral ligands for asymmetric catalysis. These includes helical ligands, chiral monophosphines, chiral tridentate ligands and novel chiral bidentate phosphines with rigid backbones. Excellent activities and enantioselectivities (up to 99 % ee) have been observed in many asymmetric reactions such as hydride transfer reaction, hydrogenation, alkylation of aldehydes, cycloaddition and allylic alkylation. Seven patents have been filed and several companies (Catalytica and Pfizer) have licensed this technology for the production of chiral molecules in industrial scales. Using these methods and other organometallic methodologies, we have made a number of chiral liquid crystals and related materials.

We have observedunprecedented high enantioselectivities in Rh-catalyzed hydrogenation of cyclic enamides (*J. Org. Chem.* **1999**, *64*, 1774) and cyclic enol acetates (*Angew. Chem. Int. Engl. Ed.* **1999**, *38*, 516). We have achieved the highest enantioselectivity in Rh-catalyzed hydrogenation of 3-aminoacrylic acid derivatives for the practical synthesis of chiral β-aminoacids (*J. Org. Chem.* **1999**, *64*, 6907). Also in very recent work we have accomplished the first highly enantioselective Pd-catalyzed asymmetric cyclocarbonylation of allylic alcohols to γ-butyrolactones (up to 97 % ee) (*J. Am. Chem. Soc.* **1999**, *120,* 3817) and have made major progress toward Rh-catalyzed [4+2] asymmetric cycloisomerization reactions (up to 99 %ee).

Further evidence of our creativity is high productivity in developing innovative chiral ligands and new reactions. While he has already invented three major classes of chiral ligands (PennPhos, BICP and Ambox), his group has recently developed five new ligand systems (Binaphane, HydroPhos, P, N ligands, TunaPhos and DIOP*). These effective ligands further broaden the scope of many asymmetric reactions and will have many practical applications. The new P, N ligand was used for asymmetric Michael additions of acyclic enones and gave unprecedented high enantioselectivities (*Angew. Chem. Int. Ed.* **1999**, *38*, 3518). Chelating hydroxyl phospholanes or DIOP* were prepared from a cheap starting materials (D-mannitol) and these ligands show superior properties compared to DuPhos ligands (submitted to JACS). A Rh-binaphane catalysts is highly efficient for hydrogenation of simple enamides (*Organic Lett.* **1999**, *1*, 1679). In a related study, a Rh-ferro-binaphane complex is invented as one of the most effective catalyst for hydrogenation of imines (submitted to JACS). Furthermore, Ru-ambox complexes have been developed as effective direct hydrogenation catalysts for reduction of simple ketones and high enantioselectivities have been achieved (submitted to Angew. Chem.). A Ru-TunaPhos complex is an excellent catalyst for asymmetric hydrogenation of beta-keto esters (submitted to Angew Chem.). Unprecedented highly efficient kinetic resolution (S > 60) has been achieved in a Pd-catalyzed asymmetric allylic alkylation reaction. Highly diastereoselective and enantioselective cyclopropronation have been achieved with a new Ru catalyst. The first Rh-catalyzed ene reaction is discovered and the highly enantioselective ene reaction is achieved (submitted to JACS).

We are developing high polarization materials as candidates of novel ferroelectric liquid crystals. The viscosity of a diphenyl-diacetylene liquid crystals is far lower than the corresponding quadra-phenyl liquid crystals. We have synthesized chiral liquid crystals using this conjugated backbone (diphenyl diacetylene). We also plans to change the arrangement of the phenyl-acetylene modules and these changes could alter the physical properties of liquid crystals in useful ways (e.g., absorption efficiency of Laser lines). This research is carried out in collaboration with Professor Jay Patel in Department of Physics and Professor I. C. Khoo in Department of Electrical Engineering at Penn State University. The research collaboration with Professor Khoo has resulted in excellent laser optical limiting materials.

Brief summary of plans for future work

The major goals of future work are to continue the development of chiral synthesis technology and to strength the collaboration with Professor I. C. Khoo through extensive synthetic work of ferroelectric liquid crystals and nonlinear optical liquid using our methods. The aim of this project would be to understand at a fundamental level the origin of the electroclinic effect in chiral smetic liquid crystals so that the effect can be enhanced to make useful optical devices such as novel electro-optic modulators for fiber-optic applications. A primary target is to synthesize chiral materials with smectic A phase with electroclicic effect. The proposed research would result in a low cost fiber optic based optical modulator that operates on microsecond to possibly nano-second time scale for a variety of commercial and military applications. The collaboration with Professor Khoo focuses on development of nonlineear optical liquid cored fiber array and liquid crystal film for ps-cw frequency agile laser optical limiting applications.

List of names of graduates students and post-doctorals currently working on the project

Dr. Zhaoguo Zhang

Dr. Wenge Li

Dr. Qian Hu

Mr. Jim Longmire

Ms. Ping Cao

RESEARCH HIGHLIGHTS OF XUMU ZHANG'S WORK

Recent work in Zhang's research group on asymmetric catalysis was cited by the *Chemical & Engineering News* (July 14, 1997, and October 20, 1997). Following the coverage of Jacobsen's enantioselective catalysts for hydrolysis of epoxides, Stinson wrote that "*another hot intellectual property* among academically invented chiral catalysts is the so-called PennPhos of organic chemistry Professor Xumu Zhang at Penn State". The work was also covered by *Genetic Engineering News* (October 15, 1997). Dr. De Palma wrote: "two recent discoveries represent *major steps toward practical asymmetric catalytic reaction* by Harvard Professor Eric Jacobsen's 'hydrolytic kinetic resolution' and Penn State Professor Xumu Zhang's chiral phosphines for asymmetric hydrogenation reactions." In a *Chemtract* article, Professor Dai comments that the principles underlying the design of new chiral ligands discussed in Zhang's work is *inspiring to the further advancement of asymmetric synthesis*. Zhang's chiral ligands (e.g., BICP) will be influential members in the family of useful chiral ligands such as BINAP and DuPhos. In the *Centre Daily Times*, Hopkins wrote that Zhang's catalyst allows for more efficient and less costly production of molecules with the desired handiness (chirality). In the Catalytica press release, Dr. James A. Cusumano, CEO, said: "we see this technology as offering a *significant potential benefit* for the production of pharmaceuticals for which only one specific chiral form of the drug molecules is of therapeutic interest." The Rh-PennPhos work was highlighted by Dr. Rudiger Selke in *Angewardte Chemie International Ediction,* **1998**, 37, 1827. Dr. Selke described that the young research group of Zhang at Pennsylvania State University has *climbed a mountain* that has long defied all attempts at scaling its peak-the complex-catalyzed, highly enantioselective hydrogenation of purely aliphatic ketones. Dr. Selke regards the work done by Xumu Zhang's group has a similar impact as the research conducted by R. Noyori. in asymmetric hydrogenation of simple ketones. Recently, Zhang's benchmark results on asymmetric carbonylation have been highlighted in the *Chemical Engineering News* (August 30, 1999).

Principal Investigator: Xumu Zhang
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Brief summary of plans for next years work

The major goals of next years work are to continue the development of chiral synthesis technology and to strength the collaboration with Professor Jay Patel and Professor I. C. Khoo through extensive synthetic work of ferroelectric liquid crystals using our methods. The aim of this project would be to understand at a fundamental level the origin of the electroclinic effect in chiral smetic liquid crystals so that the effect can be enhanced to make useful optical devices such as novel electro-optic modulators for fiber-optic applications. A primary target is to syntehsize chiral materials with smectic A phase with electroclicic effect. The proposed research would result in a low cost fiber optic based optical modulator that operates on microsecond to possibly nano-second time scale for a variety of commercial and military applications.

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Dr. Guoxin Zhu

Dr. Qiong Zhong Jiang

Mr. Jim Longmire

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Xumu Zhang

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University Park, PA 16802

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Zhang, Xumu

14. Abstract

During the funding period, we have made significant progress both in the developing new methods for asymmetric synthesis and discovering new liquid crystal materials. Over a dozen of papers have been published or in press in several journals (J. Am. Chem. Soc., J. Org. Chem. and Tetrahedral Letter) and three have been submitted for publication. We have developed a chiral toolbox with a large set of chiral ligands for asymmetric catalysis. These includes helical ligands, chiral monophosphines, chiral tridentate ligands and novel chiral bidentate phosphines with rigid backbones. Excellent activities and enantioselectivities (up to 99 % ee) have been observed in many asymmetric reactions such as hydride transfer reaction, hydrogenation, alkylation of aldehydes, cycloaddition and allylic alkylation. Seven patents have been filed and several companies (Catalytica and Pfizer) have licensed this technology for the production of chiral molecules in industrial scales. Using these methods and other organometallic methodologies, we have made a number of chiral liquid crystals and related materials. We are developing high polarization materials as candidates of novel ferroelectric liquid crystals. The viscosity of a diphenyl-diacetylene liquid crystals is far lower than the corresponding quadra-phenyl liquid crystals. We have synthesized chiral liquid crystals using this conjugated backbone (diphenyl diacetylene). We also plans to change the arrangement of the phenyl-acetylene modules and these changes could alter the physical properties of liquid crystals in useful ways (e.g., absorption efficiency of Laser lines). This research is carried out in collaboration with Professor I. C. Khoo in Department of Electrical Engineering at Penn State University. The research collaboration with Professor Khoo has resulted in excellent laser optical limiting materials.